Provide aqueous solution containing 0.1-50% by weight of alkaline cleaning agent and 0.001-10% of sequestering agent, e.g., sodium glucoheptonate.

With this solution, fill portions of paper mill system to be cleaned.

Circulate the solution through such portions at elevated temperature below 212°F.

Remove the solution from the system, leaving surface areas of the system free from deposits of polyvalent metal hydroxides but with a material deposit of the sequestering agent.

Place paper mill in operation for production of paper, the deposit of sequestering agent preventing deposit of objectionable amounts of polyvalent metal compounds on such surface areas from the circulating water of the paper mill.

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This invention relates to the operation of paper mills and particularly to an improved method for preparing paper mills for operation, and to a novel paper mill "boil out" composition employed in such method.

During the operation of paper mills, very substantial amounts of deposited materials collect on the surfaces of the liquid circulating system of the mill and it is necessary to shut the mill down occasionally to remove such deposits. The usual method of removal is the "boil out," involving pumping a hot caustic solution through the liquid circulating system of the mill, the caustic being employed to dissolve the deposits so that the same are removed by the flowing solution.

We have observed that the troublesome deposits which form in paper mill circulating systems are mainly those of calcium and iron. We have also discovered that the conventional "boil out" methods, while having considerable effectiveness in removing some of the deposits, actually have a tendency to promote further troublesome deposits when the mill is placed into operation following the "boil out" procedure. This results because the hydroxides of the polyvalent amphoteric metals are precipitated onto the walls and surfaces of the equipment and because traces of the alkaline components of the "boil out" solution remain on the equipment. Thus, while the conventional method may leave the solid surfaces of the circulating system apparently "clean," the presence of the hydroxides of the polyvalent amphoteric metals, and the alkaline "boil out" components, on the apparently clean surfaces brings about a speedy and voluminous deposit of dioldion compounds from the circulating water in the mill during paper-making operation.

We have also observed that, among the hydroxides left on the apparently clean surfaces by the conventional "boil out" methods are those of iron and that the presence of iron is exceedingly objectionable. This is because the deposits formed during operation of the mill will include a material amount of the iron left by the "boil out" procedure and this iron will then feed sulfate bacteria, with the result that some of the deposits built up in the circulating system during the paper-making operation are of very dark color. After a time, some of these dark deposits begin to break away, flowing with the recirculating waters of the mill and thus being introduced into the paper being made, with the result that the paper is spoiled.

We have discovered that the foregoing disadvantages can be successfully overcome by carrying out the "boil out" method with a hot aqueous solution of (1) an alkaline cleaning agent substantially free from added compounds of calcium, and (2) an effective proportion of a sequestering agent capable of sequestering calcium, iron and other polyvalent amphoteric metal ions but incapable of effectively sequestering sodium, potassium or ammonium. When both the alkaline cleaning agent and such a sequestering agent are employed, the polyvalent metal hydroxides which normally precipitate from the "boil out" solution are tied up by the sequestering agent. Additionally, after the "boil out" is completed, a material amount of the sequestering agent is left on the solid surfaces of the various parts of the mill forming the circulating system, so that the tendency toward precipitation of polyvalent metal compounds, once the mill is put back into use, is eliminated or greatly reduced.

Since the sequestering agent employed must, on the one hand, be capable of effective removal of the polyvalent metal ions always present in the "boil out" water, while, on the other hand, not acting to decrease the effectiveness of the alkaline cleaning agent, it is apparent that the sequestering agent must be carefully selected. We have found that, while many commercially available sequestering agents are unsatisfactory for use in "boil out" compositions, highly satisfactory results are obtained if the sequestering agent is selected from the group consisting of the sugar acids, the alkalii metal, alkaline earth metal and ammonium salts of the sugar acids, and sorbitol.

Of this class of compounds, the gluconates are unusually advantageous, sodium gluconate being a particularly effective agent. Other typical compounds which may be used are gluconic acid, sodium gluconate, saccharic acid and potassium sodium saccharate.

The alkaline cleaning agents useful in accordance with the invention include sodium hydroxide, which is particularly effective, potassium hydroxide, sodium carbonate, the various phosphates and polyphosphates of sodium or potassium, ammonium hydroxide, the silicates of sodium or potassium, sodium metsilicate being particularly useful, and the soaps, such as sodium oleate, sodium stearate and the usual saponified fatty glyceride mixtures of commerce. For paper mill situations of usual severity, sodium hydroxide or potassium hydroxide are frequently the most feasible alkaline cleaning agents.

Advantageously, we first prepare a "boil out" composition comprising at least one of the alkaline cleaning compounds and the special sequestering agent, the latter being included in proportions equal to 1–20% of the weight of the alkaline compound employed. Such composition is then added to the "boil out" water to provide a solution in which the concentration of the alkaline cleaning compound is 0.1–5.0% by weight. Thus, the concentration of the special sequestering agent is 0.001–1.0% by weight.

Such compositions can be either aqueous solutions or dry mixtures. In the case of solutions, the alkaline cleaning compound can be employed in proportions equal to 3–50% by weight of the total composition, with the proportion of sequestering agent equal to 0.3–10% by weight. In the case of dry mixtures, and assuming no additional ingredients, such as extenders, etc., the system of alkaline cleaning composition comprises 50–99% by weight of the alkaline cleaning compound and 1–20% by weight of the special sequestering agent.

Whether liquid or dry mixture, the compositions can advantageously include a substantial proportion of an insoluble inorganic abrasive material capable of aiding the "boil out" solution in removing deposits. Bentonite and other clay-like minerals are especially effective. When the "boil out" composition is prepared as an aqueous solution, the bentonite or like abrasive material can be employed in amounts up to 5% by weight of the composition. When a dry mixture is employed, the bentonite or the like can be employed in amounts up to about 10% of the combined weight of alkaline cleaning compound and sequestering agent.

The alkaline cleaning compound and special sequestering agent, or the composition containing the same, can be added to the "boil out" water either before or after the water is introduced into the circulating system to be cleaned, and the water is then heated to the temperature desirable for circulation through the system. Alternatively, the water can be introduced into the system and then heated, the alkaline cleaning compound and special sequestering agent being introduced into the hot water. The solution is passed through the circulating system at
an elevated temperature below the boiling point, advantageously at least about 180° F. While normal "boil out" methods call for circulation times on the order of several hours, these times can be considerably reduced when employing the present invention, though it will be understood that the duration of treatment will of course vary, depending upon the severity of the situation encountered in the mill. It will also be understood that the volume of solution employed is dependent upon each particular case. All that is required is that a sufficient amount of solution be employed to fill those portions of the system through which the solution is to be circulated.

Thus, the method of the present invention is carried out in accordance with the flow sheet constituting the single figure of the accompanying drawings.

The following examples are illustrative:

**Example 1**
A paper mill which has been shut down because of the occurrence of extensive deposits on the walls of the liquid circulating system is treated as follows: 5,000 gallons of water is introduced into a stock storage chest and heated to 180° F. by the introduction of live steam. During heating of the water, sodium hydroxide and a mixture of sodium glucoheptonate and b-sodium glucoheptonate are added at rates providing a solution containing 1% by weight of the basic and 0.5% by weight of the sequestering agent. When the solution has been adequately heated, it is continuously circulated, by the pumps of the circulating system, through the circulating system for a period of four hours. During such circulation, the deposits on the walls of the circulating system are gradually removed. The "boil out" solution is then pumped out of the system and the paper mill put promptly into operation.

Where, employing ordinary "boil out" procedures, with out the special composition of this example, it would normally be necessary to run the mill for as much as 8–10 hours on start-up before obtaining salable paper, the mill treated in accordance with this example can be put into successful operation much more promptly, the start-up time being limited, under normal circumstances, to that required for obtaining proper operation without giving consideration to the effect of "boil out" residues.

**Example 2**
The procedure of Example 1 is repeated, adding the sodium hydroxide at a rate providing a concentration thereof of approximately 4% and adding the sequestering agent at a rate providing a concentration thereof of 1%. The time for circulation of the "boil out" solution so prepared is shortened to two hours in view of the increased concentration of the caustic and sequestering agent.

In both of the foregoing examples, it will be found that the objectionable deposits are much more readily and completely removed than in the case of conventional "boil out" methods. The danger that some deposits will be only partially treated, and will thus break loose during the start-up of the mill, is accordingly substantially eliminated. It will also be found that there is much less tendency toward formation of deposits early in the operation of the paper mill, after the "boil out" treatment, and that there is less tendency toward occurrence of sulfate bacteria.

As a general rule, depending upon the severity of the conditions encountered in the mill, better cleaning of the circulating system, and longer successful operation of the mill in the making of paper following cleaning, are obtained when the proportion of the special sequestering agent is increased.

**Example 3**
The procedure of Example 2 is repeated, using potassium hydroxide as the caustic material and employing the same proportions of caustic and sequestering agent. Again, successful cleaning is accomplished in a relatively shorter time than is usually employed, and the surfaces of the system are left substantially free of precipitated hydroxides.

**Example 4**
The procedure of Example 1 is repeated, using sorbitol as the sequestering agent and increasing the amount thereof to provide a sorbitol concentration of 1% by weight. The results are equivalent to those obtained in Example 1.

**Example 5**
A liquid "boil out" composition is prepared by dissolving 30 parts by weight sodium hydroxide and 3 parts by weight of mixed a-sodium glucoheptonate and b-sodium glucoheptonate in 67 parts by weight water. This composition is used to clean a paper mill by feeding the liquid composition into a stock storage chest filled with water, heating the water to between 180° F. and 200° F., and circulating the resulting solution through the recirculating system of the mill. The composition is added to the stock chest at a rate equal to 10% of the water therein, so that the concentration of sodium and glucoheptonate in the "boil out" water is 3% and 0.3% of the glucoheptonate, 0.3%, by weight. This procedure gives a thorough removal of deposits in a relatively shorter time than has been usual for conventional "boil out" compositions, leaving the system substantially free of precipitated hydroxides.

**Example 6**
A dry "boil out" composition is prepared by blending 80 parts by weight sodium hydroxide and 20 parts by weight of mixed a-sodium glucoheptonate and b-sodium glucoheptonate. The composition is transported as dry mix to the point of use and then introduced into the "boil out" water after the same has been placed in the system and heated. Both compounds being highly soluble, agitation, other than by circulation of the water, is ordinarily not required. The dry composition is added in such amount as to provide a concentration of the sodium hydroxide on the order of 2–3%, and of the glucoheptonate, 0.5–0.75%, by weight, for normally severe deposits in the mill.

**Example 7**
Example 5 is repeated, employing in addition to the glucoheptonate and sodium hydroxide an amount of bentonite equal to 5% by weight of the liquid composition. The composition is employed in the same manner as in Example 5. Including bentonite as an abradant, the composition acts more quickly in those cases where the deposits in the circulating system of the mill are encrusted and unusually tenacious.

**Example 8**
Example 6 is repeated, employing in the dry mixture 10 parts by weight bentonite. The dry composition is employed as in Example 6, but is more rapid in its cleaning action than the composition of that example when encrusted and unusually tenacious deposits are encountered.

We claim:
1. The method for preparing the liquid circulating system of a paper mill for use comprising providing in the system an aqueous solution containing 0.1–5.0% by weight of at least one alkaline cleaning agent and 0.001–1.0%, by weight of at least one sequestering agent selected from the group consisting of the sugar acids, the alkali metal, alkaline earth metal and ammonium salts of the sugar acids, and sorbitol, the volume of such solution being such as to substantially fill those unitary portions of the paper mill system to be cleaned, then circulating said solution at an elevated temperature below 212° F. through those portions of the system to be cleaned, removing the solution from the system and thereby leav-
ing surface areas of the system substantially free from deposits of polyvalent metal hydroxides but with a material deposit of such sequestering agent, and then placing the mill into operation for production of paper, the presence of said material deposit of such sequestering agent being effective to prevent the deposit on said surface areas of objectionable amounts of precipitated polyvalent metal compounds from the circulating water in the mill when the mill is placed in operation.

2. The method for preparing the liquid circulating system of a paper mill for use comprising introducing into the liquid circulating system a volume of water sufficient for circulation through those portions of the system to be cleaned, incorporating into the water at least one alkaline cleaning agent and at least one sequestering agent selected from the group consisting of the sugar acids, the alkali metal, alkaline earth metal and ammonium salts of the sugar acids, and sorbitol, in proportions sufficient to provide a solution containing 0.1-5.0% by weight of said cleaning agent and 0.001-1.0% by weight of the sequestering agent, heating the water to 180-200° F., circulating the resulting hot solution through those portions of the system to be cleaned, removing the solution from the system and thereby leaving surface areas of the system carrying a small but material amount of said sequestering agent but substantially free from deposits of polyvalent metal hydroxides, and then placing the mill into operation for the production of paper, the presence of said material amount of said sequestering agent being effective to prevent the deposit on said surface areas of objectionable amounts of precipitated polyvalent metal compounds from the circulating water in the mill when the mill is placed in operation.

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